

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:  
Erik JANZEN *et al.*

Appl. No.: 10/830,047

Confirmation No.: Not Yet Assigned

Filed: April 23, 2004

For: DEVICE AND METHOD FOR  
PRODUCING SINGLE  
CRYSTALS BY VAPOR  
DEPOSITION

Art Unit: Not Yet Assigned

Examiner: Not Yet Assigned

Atty. Docket No.: 35947-202834

Customer No.

26694

PATENT TRADEMARK OFFICE

**Submission of Certified Copy of Priority Document**

Commissioner for Patents  
P. O. Box 1450  
Alexandria, VA 22313-1450

Sir:

Submitted herewith is a certified copy of Application No. 0301225-9 filed on April 24, 2003 in Sweden, the priority of which is claimed in the present application under the provisions of 35 U.S.C. 119.

Date: 5-19-04

Respectfully submitted,

Eric J. Franklin  
Registration No. 37,134  
VENABLE LLP  
P.O. Box 34385  
Washington, D.C. 20043-9998

Telephone: (202) 344-4000

Telefax: (202) 344-8300

# PRV

PATENT- OCH REGISTRERINGSVERKET  
Patentavdelningen

## Intyg Certificate

Härmed intygas att bifogade kopior överensstämmer med de handlingar som ursprungligen ingivits till Patent- och registreringsverket i nedannämnda ansökan.

*This is to certify that the annexed is a true copy of the documents as originally filed with the Patent- and Registration Office in connection with the following patent application.*



(71) Sökande                      *Okmetic Oyj, Vantaa FI*  
Applicant (s)

(21) Patentansökningsnummer    *0301225-9*  
Patent application number

(86) Ingivningsdatum                      *2003-04-24*  
Date of filing

*Stockholm, 2004-04-30*

*För Patent- och registreringsverket*  
*For the Patent- and Registration Office*

*Hjärdís Segerlund*

Avgift  
Fee                      *170:-*

Int. t. Patent no. 97/00000

1997-04-24

Patent Office of Sweden

1

## Device and method for producing single crystals by vapour deposition

### Field of the invention

The present invention describes a device and a process to grow single crystals by high temperature deposition from a vapour phase. In particular the device can be used to produce large and high quality crystals of a) silicon carbide, b) a group III-nitride, for example GaN or AlN, or c) an alloy of SiC and a group III-nitride.

### Background and prior art

Wide band-gap semiconducting crystals such as silicon carbide (SiC), group III-nitrides such as gallium nitride (GaN) and aluminium nitride (AlN) offer several attractive electrical and physical properties for fast switching power devices and optoelectronic devices. These wide band gap semiconductor and their alloys also differentiate themselves from important semiconductors, such as silicon and gallium arsenide, by the fact that they cannot at present be directly grown from a melt or a liquid solution under practically and economically interesting conditions. Instead, ingots of SiC, GaN or AlN need to be grown from the vapour phase, by the epitaxial deposition of a supersaturated vapour flux onto a seed crystal.

In the case of SiC, the first method historically used to produce semiconductor grade SiC crystals of diameter and length sufficient to produce wafers for semiconductor applications, is the sublimation method, also known as physical vapour transport (PVT). The core concept of this method has been introduced by Lely in 1955 (Berichte der Deutschen Keramische, Ges. 32-8 p. 229 (1955) and has been modified in 1978 by Tairov and Tsvetkov (J. Cryst. Growth 52, p. 146 (1981) to produce consistent semiconductor grade SiC crystals where key properties such as the polytype, the growth rate and the diameter of the crystal can be controlled. Briefly, the method is based on the use of a sealed crucible in which a temperature gradient is established between a high temperature zone, where a solid source material such as a SiC powder is sublimed, and a lower temperature region in which the sublimed species crystallise on a seed crystal.

The sublimation method has also more recently demonstrated the ability to grown AlN crystals, whereas GaN crystals are essentially grown on hydride VPE based techniques.

The sublimation method today allows the production of SiC crystals of diameters ranging between 50 and up to 100 mm with entry quality and cost sufficient to enable devices such as LEDs and Schottky diodes for industrial applications.

5 Despite these outstanding achievements, in the sublimation technique there are several challenges, which require skill to be solved on an industrial scale. One of these may, for example, be a changing sublimation rate and a drift of the sublimed species stoichiometry during growth. Instabilities in the source material supply and drifts of the temperature distribution in the source feedstock and in the crystallisation zone will, for example, cause drifts of the growth rate and of  
10 the incorporation of doping species. If not properly controlled, such drifts adversely affect the yield of the crystal growth process. For example, to date aluminium doped p-type SiC wafers grown by sublimation exhibit high densities of micropipe defects. From a larger perspective, in a sealed PVT system, the depletion of the source feedstock limits the duration of a continuous growth  
15 process and thus the crystal length.

These challenges may be solved by further improvements of the sublimation process, and the capability of the technique, or variants thereof, to produce SiC wafers on a relatively large scale, is an indication of its industrial potential.

20 An alternative industrially interesting technique, which does provide a continuous control of the source material supply together with the potential of growing long crystals from the vapour phase has been introduced in 1995 by US patent no. 5,704,985. This technique is generically described as High Temperature Chemical Vapour Deposition (HTCVD) and differs from sealed PVT systems by making use  
25 of an open hot-wall system offering high degrees of freedom and control of the source and doping materials supply. In particular, at least one of the components of the grown material is continuously supplied in the form of a regulated gas flow and fed into a high temperature region through an inlet opening. Additionally, an exhaust is provided downstream of the crystallisation region to control the gas  
30 flow along the growing crystal surfaces and exhaust the by-products resulting from the crystallisation process. The technique may be described as Chemical Vapour Deposition (CVD) owing to its conceptual similarity with the CVD techniques used to epitaxially grow layers as thin as a few microns or less. However, as taught in US patents no. 5,704,985 and no. 6,048,398, in order to  
35 reach growth rates economically interesting for producing large crystals, the

HTCVD technique uses an order of magnitude higher source gases feed rates and several hundreds degrees higher temperatures than normal CVD processes.

For example, in a device similar to the one of the first figures of US patent no. 5,704,985 (Fig. 1), in the specific case of SiC, by heating the seed crystal (13) to a temperature of 2250 °C and feeding via inlet 15 a gas mixture containing 0,3 L/min of silane and 0,1 L/min of ethylene diluted in a helium carrier gas, a crystallisation rate of 0.5 mm/h is obtained.

However, when carrying out the method for several hours, it was rapidly experimentally observed that SiC also crystallises around the seed crystal substrate (13), onto the holder (12) made for example of graphite, and on the exposed surfaces of the exhaust holes (14) in Fig. 1. On the surfaces in the immediate vicinity of the seed crystal (13), SiC crystallises in a dense polycrystalline solid comprising mainly 6H and 15R polytypes. Further downstream, in the exhaust holes 14, SiC crystallises in somewhat less dense 3C polytype needles. The dense polycrystalline deposition can occur at a rate approximately twice that of the single crystal crystallisation rate. Further downstream, as the temperatures decreases and the supersaturation increases, 3C crystal needles nucleate and grow even more rapidly in size, eventually obstructing the gases outlet path within 2 to 4 hours. Once the exhaust path downstream of the seed crystal is sufficiently obstructed, a pressure difference rapidly builds up between the sources gases inlet 15 and the exhaust port 16. If the pressure differential is allowed to reach a few mbars, it is reproducibly noticed that a rapid deterioration of the single crystal polytype and structural quality occurs. The source gases can also start to flow along a path of higher conductance than the one of the obstructed exhaust 14, for example through any porous insulating material such as 15 in Fig. 1. The insulating properties of the material are then rapidly deteriorating due to reaction with silicon, which forces the growth to be interrupted. Alternatively, when the exhaust path 14 becomes obstructed under conditions where the source gases are not allowed to find a path of higher conductance, a very rapid blocking of the gases inlet conduct takes place by polycrystalline silicon deposition. In this case, the growth also needs to be interrupted as no source gases can be supplied to the single crystal. The parasitic deposition of polycrystalline solid phases thus leads to a catastrophic runaway of the system, forcing to a termination of the growth process before a crystal of a desired length is produced.

Inventor: Patent: 007/031

2003-04-24

Page 15 of 15

4

A tentative solution to solve this problem has been presented in the PCT application WO 98/14644. In the example of SiC crystals growth, this application describes a device where the Si and C containing process gases are separated from the main heating element 7 in Fig. 2 by a thin inner cylinder 25. A blanketing inert gas is made to flow between the main heating element and the inner cylinder, the inner cylinder ending at a distance approximately corresponding to the single crystal growth front. Downstream of the single crystal growth front, the blanketing gas guided along the walls of the main heating cylinder, is meant to prevent or substantially slow down deposition of polycrystalline SiC on the downstream inner walls and to slow down growth of polycrystalline SiC on the seed holder 13, so that the outlet path 31 remains free. A similar solution is presented in the European patent application no. 787,822 A1 where a blanketing gas flowing parallel to the process gases stream is presented for a device operating between 800 and 2500 °C.

It has been found that such a solution, as presented or derived from these documents, does not solve the problem described above to an extent sufficient to grow SiC or other crystals of a length more than a few mm. Experiments using an inert blanketing gas such as helium or argon showed that growth of 3C needles still occurred on the downstream side of the single crystal growth front. When helium is used as blanketing gas an even higher rate is easily obtained, whereas the use of argon only pushes the deposition region a short distance downstream. This unexpected result can be explained by an additional flux of carbon carried by the blanketing gas when it passes along a graphite made uncoated heating element and by the differing thermal conductivity of the two considered gases. In a silicon rich exhaust gas mixture, any additional carbon supply leads to an increase of the downstream growth of polycrystalline SiC. A similar phenomena is observed when using a heating element 7 coated with SiC. To circumvent this phenomena, it will be obvious to a person skilled in the art to use, as an improvement, a heating element and guide cylinder either made of a metal carbide or of graphite coated with a metal carbide such as for example TaC or NbC. Preferably the exposed surfaces will also have a low surface roughness to offer less nucleation sites to polycrystalline SiC. Under typical process conditions leading to a single crystal growth rate of the order of 0.5 to 1 mm/h, it is however observed that such a design only leads to a further downstream

location of the uncontrollable 3C-SiC deposition. This small improvement of the blocking time is not sufficient to continuously grow several cm long crystals. Moreover, the use of metal carbide coated parts represents a substantial additional cost of the manufacturing process.

5

In other prior art devices designed to grow SiC crystals where at least one component of the material to be grown is fed as a gas and the by-products of the process are exhausted through an outlet, no solution to parasitic deposition of the polycrystalline form of the material to be grown is mentioned. For example, European patent 554,047 B1 teaches the growth of SiC crystals by a device using silane and propane as source gases which react in a first reaction zone to form SiC particles to be subsequently evaporated in a lower pressure sublimation zone. The by-products of the crystallisation process and the carrier gas are just said to be exhausted through an outlet. In US patent 5,985,024, filed in 1997, a device is disclosed where silicon vapour is supplied from a heated silicon melt and an hydrocarbon gas such as propane is supplied into the growth zone through a gas supply inlet. In this device, the excess gas downstream of the growing SiC ingot is also just said to be removed from the growth zone by means of a passageway, or outlet channel. Owing to the required temperature distribution in the seed holder to allow the growth of a SiC crystal to take place, it is believed that such passageways will inevitably be subject to a catastrophic blocking by either polycrystalline SiC, pyrolytic graphite or polycrystalline Si deposition. A similar concept is described in US patent 6,048,398 filed in 1995 where a molten silicon feedstock in combination with a hydrocarbon gas can be used as source gases. The excess gases are exhausted downstream of a seed crystal holder which is rotated and pulled as the single crystal growth proceeds. Despite a beneficial cleaning action of polycrystalline deposits induced by the rotation of the seed holder, such a mechanical cleaning induces stresses in either the rotation mechanism or the seed holder and the elements coming in contact with it. This can lead to mechanical failure of any of the above mentioned parts.

In US patent application no. 2002/0056411 A1, a high temperature vapour deposition apparatus to produce SiC ingots is discussed where the pressure of the gas mixture in the growth region is set higher than that of the exhaust gas mixture to increase the yield of the process. This pressure difference can be achieved by designing the apparatus so that the conductance of the inlet is made



higher than the one of the outlet. After a low conductance situated downstream of the single crystal growth zone, the decreased pressure of the exhaust gas mixture causes, at constant temperature, a decrease of the deposition rate of parasitic polycrystalline material. This slows down in any catastrophic blocking along the path downstream of the conductance reduction zone of the exhaust mixture. However, as pointed out in the cited application, as the temperature decreases along this downstream path, deposits accumulate in a given region termed as gas trap. Preventing such deposits even in a controlled region would allow to continue the process for a longer time and thus produce longer crystals. Moreover, in this application, the system must be operated at a reduced pressure at least in the downstream part of the conductance reducing region. It can be desirable to instead operate the device at substantially atmospheric pressure, both in the growth zone and in the outlet zone, as this can favour both higher yields and lower cost of the complete system.

The origin of the problem described above is in a sense a fundamental, as even if the maximum mass transport of reactants is arranged around the growing crystal, the high process temperature (2000-2400 °C) requires to continuously supply seed temperature dependent amount of Si vapour, which will not be crystallised, to compensate for the continuous Si evaporation from the heated crystal.

Patent- och  
2003-04-24

7

Patent- och

### **Purpose and summary of the invention**

This invention provides a method and a device to grow at a high temperature in a heated room (called susceptor or crucible), from the vapour phase, a single crystal of either SiC, a group III-nitride, or alloys thereof, at a growth rate and for a period of time sufficient to produce a crystal of several millimetres, or preferably several centimetres, length.

In particular, it is an object of this invention to slow down or eliminate the formation of polycrystalline and other solid deposits downstream of the single crystal crystallisation area to avoid a partial or complete obstruction of a susceptor exhaust path by a gas mixture fed to the crystallisation area. A correlated purpose of the invention is to control the diameter of the growing single crystal and prevent growth of polycrystalline material around it, thereby preventing crystalline defects generation during the high temperature growth phase and during the subsequent cooling phase.

A further object of the invention is to decrease the concentration of unwanted metallic impurities in the epitaxially grown material by removing from the vapour phase active metallic elements released by parts heated downstream of the crystallisation area.

To prevent the formation of undesirable polycrystalline deposits on surfaces in the vicinity and in any region downstream of the single crystal growth area, the invention proposes to lower the local supersaturation of at least one component of the material grown by introducing, in the vicinity of these surfaces, a separate gas flow having the chemical property of etching the material grown. In the case of SiC or GaN crystal growth, a gas flow containing at least one halogen element such as hydrogen chloride, chlorine or a mixture of hydrogen and either chlorine or hydrogen chloride is preferably used as etchant. As will become apparent from the detailed description of the invention, other gases or gas mixtures containing halogens such as Br, F or I may also be used for a similar purpose. The etching gas may also be distributed in such a manner to actively control the shape of the growing crystal. Further preferred features and advantages of the invention are made apparent and described in the following drawings, description and claims.

Int. Patent No. 01/031

2003-04-24

Page 1 of 1

8

### Brief description of the drawings

Figure 1 illustrates a prior-art HTCVD growth device.

5 Figure 2 illustrates another prior-art HTCVD growth device.

Figure 3 is a cross section of a device according to the invention.

Figure 4 is a cross section of a modified device according to the invention.

10

Figure 5 shows the ratio of supersaturation of the SIC (top graph), carbon (middle) and silicon (bottom) condensed species with a  $[Cl]/[H]$  ratio of 0.5.

15

Figure 6 shows the ratio of supersaturation of the SIC, carbon and silicon condensed species with a  $[Cl]/[H]$  ratio of 1.2.

011/031

**Detailed description of the invention**

Fig. 3 schematically shows an improved device comprising a growth chamber of a HTCVD system based on the concepts described in the US patents no. 5,704,985, 6,039,812 and 6,048,398. This device will also be described here as the device of the invention may have a similar principle construction as in the above mentioned documents but differs in the particular features and improvements described in the present invention. The device of Fig. 3 is suited to grow single crystals of SiC, a group-III nitride such as GaN. Some parts are for the sake of simplicity schematised and it is obvious to a person skilled in the technical field that the device also comprises elements such as mass flow controllers, valves, pumps, control electronics, purifiers, a scrubbing system and other elements, as is common practice in CVD systems.

The high temperature chemical vapour deposition device comprises a casing 1 constituted, for example, of a single wall quartz tube 2 tightly mounted between a lower flange 3 and an upper flange 4. Each flange comprises a fixed casing 3a and 4a and a movable lower lid 3b and upper lid 4b which can be lowered or lifted, respectively, to access the interior of the casing 1 for loading and unloading the hot-zone of the device. The casing 1 may alternatively be constituted by a double wall water cooled quartz tube or can be surrounded by a water cooled stainless steel casing (not shown). The interior of the casing 1 comprises a heater 7, also called susceptor or crucible in the literature, and is surrounded by a low conductivity thermally insulating material 10 such as carbon felt or other forms or materials compatible with the temperature range of the process and its heating means. The heater 7 is axis symmetric and is made of a material compatible with high temperatures such as uncoated or coated graphite, a metal carbide or nitride, or a combination thereof. The heater may be of cylindrical shape, however, the diameter of the heating element may axially vary to converge in certain regions or diverge in other regions to achieve a specific gas flow pattern or a specific spatial temperature distribution in the heater 7 and in the vicinity of the crystal holder 12. The susceptor 7 is heated either by RF induction through a coil 11, or by resistive heating, to a temperature above 1900 °C (and preferably in the range of 2000°C to 2600°C) for SiC crystal growth, or above 1200 °C (at least 1100 °C and preferably in the range of 1200 °C to 2200 °C ) for GaN crystal growth. A seed crystal 13 is mounted by mechanical or chemical means to a seed holder 12 which is physically attached

to a shaft 16 having at least one hollow conduit through which the temperature of the seed holder can be measured by an optical pyrometer or thermocouple(not shown). To obtain a preferential crystallisation on the seed crystal surface rather than on the surface 26 of the susceptor 7, the seed holder is maintained at a lower temperature than the surface 26, thereby establishing a temperature gradient. The crystallisation process is carried out by feeding a vapour phase containing the elements of the material to be grown through the heated susceptor 7 towards the seed crystal. The elements amounts of the crystal to be grown are chosen so that the heated vapour becomes supersaturated when reaching the crystallisation front, here called the growth front 25a. In the specific case of SiC growth, the susceptor 7 is heated to temperatures ranging from 2100 to 2600 °C while the seed holder is maintained at temperatures ranging from 200 to 2400 °C, depending on the source material feeding rate and its C/Si ratio, the polytype and the crystallographic orientation of the seed crystal. A preferred source material for growth of SiC ingots consists of a  $\text{SiH}_x\text{Cl}_y$  gas or liquid ( $x=0$  to 4,  $y=0$  to 4) and an hydrocarbon such as methane, ethylene or propane. As described in US patent no. 6,039,812, the Si containing gas or liquid is fed through an inner conduit 22. The hydrocarbon gas may either be fed in the same inner conduit 22 or in a concentric annular conduit 23 surrounding said inner conduit 22 and delimited by a water cooled stainless steel flange 21 part of the lower lid 3b. A carrier gas such as hydrogen, helium, argon or a mixture thereof is also fed into conduit 23 and exhausted downstream of the growth front 25a via an outlet channel 14.

In order to prevent deposition of polycrystalline silicon carbide along the surfaces 26 and 27 of the exhaust channel 14, the device comprises additional delivery means such as channels emerging in the vicinity of the single crystal growth zone or in any downstream heated part exposed to Si and C containing gases. A gas mixture having the property of chemically etching SiC is fed through these additional channels. It has been found that the etching gas mixture shall in the case of SiC growth include at least one halogen element to neutralise the Si containing vapour species. The etching gas mixture preferably also has the property to react with carbon containing vapour species, such as hydrogen. Efficient etching gas mixtures providing the desired result have been found to be gases such as chlorine ( $\text{Cl}_2$ ), hydrogen chloride ( $\text{HCl}$ ) or a mixture of hydrogen ( $\text{H}_2$ ) and hydrogen chloride or chlorine. A gas mixture containing halogens such

as fluorine (F) or iodine (I) and hydrogen also achieves the desired etching effect.

To provide etching rates comparable to the growth rates of monocrystalline and polycrystalline SiC practised in the invention (0.5 to 2 mm/h), at least one part  
5 of the etching gas is delivered before the exhaust gases are cooled down to a temperature 600 °C lower than the monocrystalline growth front 25a temperature. In order to maintain the exhaust path 14 free, the positioning of the etching gas mixture delivery means, the amounts and ratio of halogen and hydrogen gases introduced shall match the amount of Si and C containing  
10 vapour species and the temperature of the surfaces exposed to condensation and the conductance of the exhaust gap 14.

As shown in Fig. 3, a preferential delivery means is realised by delivering a controlled flow of the etch gas through the hollow core of shafts 16a and 16b into an inner cavity machined in the seed holder 12. The etch gas mixture is allowed  
15 to escape through channels or pores 28 located above the seed crystal 13 and mix with the Si and C containing vapour having passed the growth front 25a.

The etch gas mixture is thereby heated to a temperature similar to the seed holder temperature, typically 2000 to 2400 °C, and thus very efficiently reacts with the Si and C containing vapour species. It may be noted that a plurality of  
20 delivery configurations can be used in the seed holder 12 in order to achieve an even distribution of the etch gas. For example a plurality of circumferential holes with a diameter ranging from 0.1 to several mm may be distributed along the outer surface 26 of the seed holder 12. A high porosity ring may also be used, provided it is made of a high temperature resistant material chemically inert to the etch gas mixture (e.g. graphite when a pure halogen gas such as F<sub>2</sub> or Cl<sub>2</sub> is used). An important advantage of this first delivery means is that, as the shaft  
25 16 is translated upwards at a rate similar to the SiC ingot 15 growth rate, by a pulling unit (not shown), the etch gas flow is delivered at a fixed position along the surface 27 of the seed holder assembly in relation to the crystal growth surface 25a. This allows to maintain surface 27 free of parasitic solid deposits even when the crystal grows to a length of several centimetres and is pulled a corresponding height upwards. A preferential practice of the invention includes pulling the seed holder 12 along a predetermined axial temperature profile to maintain the temperature of the crystallisation surface 25a constant as the  
30 crystal length increases. As the seed holder 12 is pulled along this temperature profile, the etch gas flow rate can be ramped over time to maintain a constant

etching rate. Another advantage of this first delivery means, is that the temperature difference between the seed holder 12 and the lower heater 7a can be increased, without provoking a higher deposition rate of polycrystalline material downstream of the single crystal 15. This can, for example, be achieved  
5 by lowering the RF power in the upstream turns 11a of the induction coil, while increasing the feed rate of the etch gas mixture into the shaft unit 16 to compensate for the higher supersaturation of Si and C containing gases.

A second delivery means for the etch gas mixture fulfilling the purposes of the  
10 invention comprises feeding the etch gas into a channel in the upper part 7b of the heater surrounding the seed crystal holder 12. The etch gas feed rate is controlled by an external flow controller 30 and fed into the casing 4a through a vacuum tight fitting connected to a quartz tube or pipe entering the upper heater  
15 7b at connection 31 for feeding an internal conduit 32. The internal conduit 32 preferably has an annular shape and communicates with exhaust channel 14 by a plurality of holes or by a porous media. The internal conduit 32 preferably communicates with channel 14 in a region where the deposit of polycrystalline solid naturally takes place in the prior art devices. In the case where the  
20 parasitic polycrystalline deposition takes place over a wide area on the surface 26, a second or several more separate channels 32 are machined into heater 7b to deliver appropriate etch gas flows over the entire surfaces desired to be kept free of such deposits. This second etch gas flow feeding system serves two purposes. The first one is to prevent the nucleation and growth of polycrystalline grains along surface 26. The etch gas flow rate may however also be adjusted to  
25 a value higher than needed for this sole first purpose to also etch the sides 25b of the growing single crystal 15. The halogen to hydrogen ratio of this second gas mixture is adjusted to value to produce a smooth mirror-like etch of the sides of the growing crystal 15. By varying the etch gas flow, the diameter of the growing crystal is controlled. In particular, a low etch flow allows the crystal to expand at a radial rate determined by the chosen balance of the etch gas flow versus the source and carrier gases feeding rate into heater 7a and the radial temperature gradient of heater 7b. The expansion rate of the crystal may be lowered or even cancelled to produce a cylindrically shaped crystal by increasing the etch gas flow rate. During this process, the shaft unit 16 is preferably rotated  
30 to produce a uniform radial etch shape.  
35

W. STROM & S. GULLIKSSON

703-04-74

Doc. No. 1000

13

- Another advantage of this second delivery means, is that in the temperature range of the invention, the use of an etch gas containing at least an halogen element such as Cl forms stable chlorides with several metallic impurities which may unintentionally be released into the source gas feed mixture. In particular,
- 5 the concentration of residual metallic impurities in the single crystal 15 could be decreased by a factor up to 100, below values detectable by state-of-the-art SIMS measurements when a small amount of Cl containing gas is allowed to diffuse to the SiC growth front 25a and 25b.
- 10 A third delivery means for the etch gas mixture fulfilling the purposes of the invention comprises feeding the etch gas along a circumferential gap formed between the inner wall of heater 7a and a concentric axis symmetric inner crucible 7c. As shown in Fig. 4, a flow of the Si and C containing source vapour is confined into the growth zone 33 until its flow sweeps across the outer surface
- 15 25b of the single crystal 15 and being exhausted into channel 14, while the etch gas flow is confined in the annular gap 34 until said etch gas flow meets the remaining Si and C containing gases in channel 14. As in the second delivery means, this third configuration of etch gas flow allows to both maintain surfaces
- 20 26 and 27 free from detrimental polycrystalline deposits while it also allows to influence the shape of the growing single crystal. A cylindrical external wall of the inner crucible 7c will be preferred to produce an essentially cylindrical ingot 15, while an external wall either diverging along the etch gas flow direction favours a concave growth front 25a.
- 25 It is in the scope of the invention to use either first, second or third delivery means described above, individually or in any combination. The invention is however best practised by using the first delivery mean during the entire duration of the process, which may extend to several tens of hours, whereas second and third delivery means may preferentially be used additionally,
- 30 separately or together, at different stages of the process. A typical example can be an crystal diameter expansion stage based of using delivery means 1 and 2 in a first stage, followed by a substantially cylindrical growth using also means 2 with a lower etch gas flow or in combination with delivery means 3.
- 35 It may be noted that these features can be used to achieve the desired solution for a variety of exhaust channel 14 configurations, such as an exhaust direction



opposite to the single crystal growth direction, as in Fig. 2, or an exhaust perpendicular to the growth direction or any intermediate angle between said opposite and perpendicular directions.

- 5 An important practice of the method taught by the present invention involves the choice of the halogen and hydrogen gas flow rates and their respective ratios. Although the authors do not wish to be bound by any theory, teaching in the method can be gained by thermodynamics considerations. These are in the following given in the Si-C-H-Cl system, however similar findings can be made  
10 for the case of III-nitrides crystal growth using for example the Ga-N-H-Cl or the Al-N-H-Cl systems.

In the following, the specific case of adding chlorine to a given Si-C-H system determined by the input source and carrier gas mixtures (for example SiH<sub>4</sub>,  
15 C<sub>3</sub>H<sub>8</sub> and H<sub>2</sub>) is given. The effect of adding Cl to the Si-C-H system is known from the prior-art in SiC CVD at temperatures in the range of 1500-1600 °C to only weakly enhance the SiC etching rate. Typical etching conditions in a prior art hot-wall CVD system involve Cl/H ratios lower than 0.03 % and show a weaker dependence of the etch rate with increasing HCl input than with  
20 increasing H<sub>2</sub> input feed rates [Zhang et al., Mat. Sci. Forums Vols. 389-393 (2002) p. 239]. In the prior-art, the etch rates are too low (less than 10 µm/h at 1600 °C) for any useful practice of the present invention. It will here be shown that the invention shall be practised under much higher Cl/H to obtain etch rates ranging from 0.3 to more than 1mm/h.

- 25 A quantification of the supersaturation decrease in the Si-C-H by addition of Cl can be quantified into a temperature drop: when Cl is added, how much can the temperature drop so that the supersaturation remains identical? The initial composition is defined from the input source Si-C-H mixture and the calculations are performed by driving the system to equilibrium. The equilibrium state is  
30 chosen as gas-phase equilibrium which represent a worse case than an equilibrium including solid Si, C and SiC phases. The experimental reality lies in between these two cases, thus the following calculations slightly underestimate the etching efficiency. A given amount of Cl is added to the system, which decreases the supersaturation of the system, by formation of e.g. chlorosilanes.  
35 The temperature is then let to drop an amount  $\Delta T$  that increases the level of supersaturation. The system is then driven to new gas phase equilibrium and

compared to the initial state. The temperature difference  $\Delta T$  corresponding to a given amount of [Cl] can then be obtained from the supersaturation (SS) isoline equal to 1 in contour plots such as the ones of Fig. 5 and 6. Along this isoline,  $SS(T, Si, C, H) = SS(T - \Delta T, Si, C, H, Cl)$ .

5 Figure 5 shows the result in the case of a system operated at a reduced pressure of 0.12 bar and a [Cl]/[H] ratio of 0.5. In particular Fig. 5 indicates that the problem of blocking channel 14 is at least partially solved in this case: the growth of solid SiC is greatly reduced and the growth of Si is stopped altogether. Unfortunately, at high temperature where the Si and C content in the gas phase  
10 is large, the effect of Cl is smaller. At 2200 °C, the Cl may allow to delay any substantial solid phase deposition along a 200 °C temperature drop  $\Delta T$ , while at 1900 °C this drop can exceed 600 °C.

Using a ratio of [Cl]/[H] higher than 1, so that a less Cl is not consumed to form HCl, the channel 14 blocking problem can be completely removed. As shown in  
15 Fig. 6 where a [Cl]/[H] ratio of 1,2 is used for the same pressure and initial composition as Fig. 5, even along a temperature drop  $\Delta T$  of 600 °C, no solid phases of SiC, or Si are possible. A solid phase of C may deposit (e.g. pyrolytic graphite) as the C supersaturation is however higher than 1. If this deposit is large enough to eventually obstruct the channel 14 within a time of 20 to 40  
20 hours, it can be removed by exercising the invention, that is by supplying an additional flow of H<sub>2</sub> in the cooler region where no more solid SiC deposit occurs. This additional flow of hydrogen may be fed in a dedicated channel going through the shaft unit 16 or in a separate channel going through the heater 7, as described earlier.

25 The large single crystals grown according to this invention may be sliced and polished into thin wafers for semiconductor applications or may be used for other applications. Depending on the intended use of the crystals, it is understood that these may be doped to achieve either low n- or p-type resistivity or made  
30 very pure to achieve a high resistivity. Dopants such as nitrogen, aluminium or other elements are preferably introduced into the growth room 33 by a controlled flow of a gas or metalorganic precursor as is commonly done in SiC CVD and group-III MOCVD of thin layers for semiconductor applications.

35 Although it has been indicated in the figures and in the above description that the flow of source gases is directed upwards (substantially against the direction

- of the local gravity vector), it is within the scope of the invention to arrange the device in the opposite direction, where the seed crystal is located at the bottom of the device, or to employ an horizontal direction, where the seed holder is either located downwards or upwards. In its present description the growth room
- 5 33 may either be maintained at a substantially atmospheric pressure or to a low pressure in the range of 50 to 800 mbar, however for other orientations of the device, a low pressure, for example less than 500 mbar, may be required to achieve the desired single crystal growth rates.
- 10 It may be noted that a person having skill and experience in the art will readily recognise that several components, shapes and process parameters may be varied or modified to a certain extent without departing from the scope and intention of the invention.



### Claims

1. A method for growing large, single polytype, compound crystals of one of  
a) silicon carbide, b) a group III-nitride c) alloys thereof, **characterized**  
in that the method comprises the steps of:
  - 5 - providing, in a heated growth enclosure comprising a seed crystal, a mixture of vapour species containing at least the elements of the compound crystal, in such a way that, at least one of the elements is continuously fed into the enclosure through an opening upstream of a growth surface of said crystal,
  - 10 - providing a separate opening downstream of the growth surface of said crystal to remove a continuous flow of remaining vapour species not having deposited under conditions yielding to growth of said crystal,
  - providing an additional gas flow containing at least one halogen element, in such a way that, said gas flow decreases a deposition rate of solid phases downstream of the growth surface of said crystal by a  
15 factor at least half of the said crystal growth rate.
2. The method according to claim 1, further comprising the steps of:
  - heating at least one region of the growth enclosure in the upstream  
20 vicinity of said crystal to a temperature of at least 1900 °C, and preferably in the range of 2000 to 2600 °C,
  - continuously feeding at least a silicon gas precursor such as silane, a chlorosilane or a methylsilane, and an hydrocarbon gas precursor towards said downstream opening,
  - 25 - providing said additional gas flow containing preferably at least Cl or F.
3. The method according to claim 2, further comprising the step of:  
providing said additional gas flow consisting of chlorine (Cl<sub>2</sub>) or hydrogen  
chloride (HCl) or hydrogen (H<sub>2</sub>) or fluorine (F<sub>2</sub>) or a mixture thereof.  
30
4. The method according to claim 1, further comprising the steps of:

13/11/03 11:11

2003-04-24

13/11/03 11:11

18

- heating at least one region of the growth enclosure in the upstream vicinity of said crystal to a temperature of at least 1100 °C, and preferably in the range of 1200 to 2200 °C,
  - continuously feeding at least a gallium or aluminium metalorganic precursor and a nitrogen containing gas towards said downstream opening,
  - providing said additional gas flow containing preferably at least Cl or I.
- 5
5. The method according to claim 4, further comprising the step of:
- 10 providing said additional gas flow consisting of chlorine (Cl<sub>2</sub>) or hydrogen chloride (HCl) or hydrogen (H<sub>2</sub>) or iodine (I<sub>2</sub>) or a mixture thereof.
6. The method according to any of claims 1 to 5, further comprising the steps of:
- 15 attaching the seed at a seed holder being mounted on a rotating and pulled shaft and feeding said additional gas flow acting as an etchant through the shaft to be delivered downstream of the growth surface of said crystal.
- 20 7. The method according to any of claims 1 to 5, further comprising the steps of:
- feeding said additional gas flow acting as an etchant into at least one channel emerging from a heated crucible into a region upstream of an initial position of the seed crystal before it is pulled for a substantial
- 25 amount of time.
8. The method according to any of claims 1 to 5, where said additional gas flow acting as an etchant is fed into a conduit formed between an outer heater and an inner crucible, said inner crucible extending along a
- 30 symmetry axis parallel to said crystal growth direction and terminating in the immediate upstream vicinity of the initial seed crystal position.
9. The method according to any of claims 1 to 5, where a carrier gas is continuously fed with the vapour species mixture containing at least the elements of the compound crystal, said carrier gas being either hydrogen,
- 35 helium or argon or a blend thereof.

10. The method according to any of claims 1 to 9, where a halogen to hydrogen ratio of the gases of any of the individual additional gas flows acting as an etchant is adjusted to a value preventing formation of solid deposits along the surface desired to be maintained free of solid deposits.
- 5
11. The method according to any of claims 1 to 10, where said additional gas flow rate acting as an etchant and its delivery means are used to control the crystal diameter, either keeping the crystal substantially cylindrical or expanding the crystal during the process.
- 10
12. A device for producing large, single polytype, compound crystals of one of a) silicon carbide, b) a group III-nitride c) alloys thereof, it comprising:
- 15
- a susceptor having circumferential walls surrounding a room for receiving a seed crystal,
  - means for continuously feeding in a vapour state or in a liquid at least one of the elements of said crystal through an opening upstream of a growth surface of said crystal,
  - means for continuously removing from the room the flow of remaining vapour species not having deposited under conditions yielding to growth of said crystal, while maintaining a predefined pressure in the growth room,
  - means for heating the susceptor and thereby the seed crystal to a predetermined process temperature
- 20
- 25 **characterised in that,** the device further comprises one of or a combination of:
- means to continuously feed and control an etching gas mixture comprising an halogen and hydrogen into a channel of a rotating shaft supporting a seed crystal holder and said channel communicating with a region downstream of the seed crystal,
  - means to continuously feed and control an etching gas mixture comprising an halogen and hydrogen into conduits designed to open into a downstream room of the susceptor, said downstream roomt being in contact with an upstream room of the susceptor extending until the initial position of the seed holder,
- 30
- 35

5 - means to continuously feed and control an etching gas mixture comprising an halogen and hydrogen into a circumferential conduit delimited by the inner wall of the upstream room of the susceptor and the outer wall of an inner crucible, said inner crucible extending along a symmetry axis parallel to said crystal growth direction and terminating in the immediate upstream vicinity of the initial seed crystal position.

10 13. The device according to claim 12, wherein said elements for growth of said compound crystal are supplied by a silane, chlorosilane or methylsilane gas source and by an hydrocarbon gas source, or by a metalorganic gallium or aluminium containing gas source and a nitrogen containing gas source.

15 14. A device according to claim 12, comprising means to independently adjust and vary over time the heating energy applied to the downstream susceptor room and the upstream susceptor room, said heating energy being supplied either by RF induction or by resistive heating or by a combination thereof.

20 15. A device according to claim 12, comprising means to vary in a controlled manner the amount and ratio of halogen and hydrogen elements in the etching gas mixture over time.

25 16. A device for producing large, single polytype, compound crystals of one of a) silicon carbide, b) a group III-nitride c) alloys thereof, it comprising:

- 30
- a crucible having circumferential walls surrounding a room for receiving a seed crystal in its upper part and a solid source, for example a powder, containing the elements of the compound semiconductor to be grown,
  - means for heating the susceptor and establishing a temperature between the source material and the seed crystal,
  - effusion openings in the crucible allowing to enhance for example the control of the stoichiometry of the vapour phase sublimed for the solid source,

35 **characterised in that**, the device further comprises means to feed or diffuse a continuous flow of a gas mixture containing at least one halogen

element in the immediate vicinity of said effusion openings so as to maintain over several tens of hours said opening free of solid deposits resulting from the condensation of the species sublimed from the source material.

024/031



### Abstract

This invention provides a method and a device to grow from the vapour phase, a single crystal of either SiC, a group III-nitride, or alloys thereof, at a growth rate and for a period of time sufficient to produce a crystal of preferably several centimetres length. Another purpose of the invention is to control the diameter of the growing crystal. To prevent the formation of undesirable polycrystalline deposits on surfaces in the downstream vicinity of the single crystal growth area, the local supersaturation of at least one component of the material grown is lowered by introducing a separate gas flow comprising at least one halogen element or hydrogen – halogen mixture.

(Figure 3)

1/6

Figures

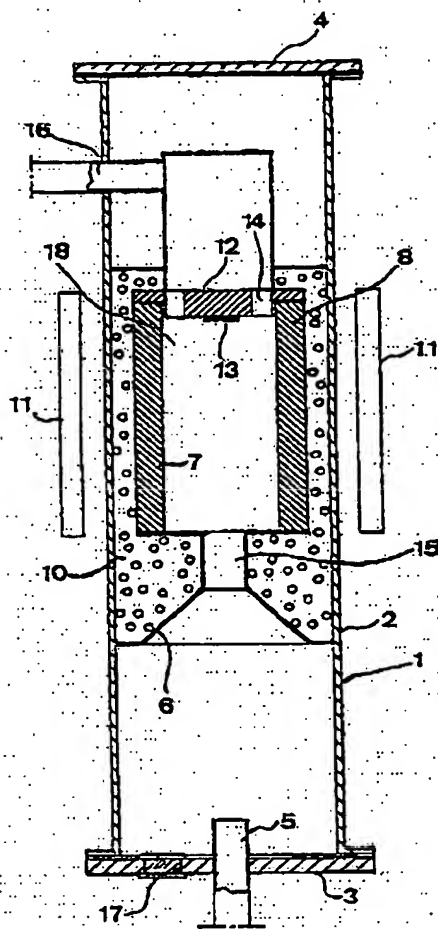


Figure 1

2/6

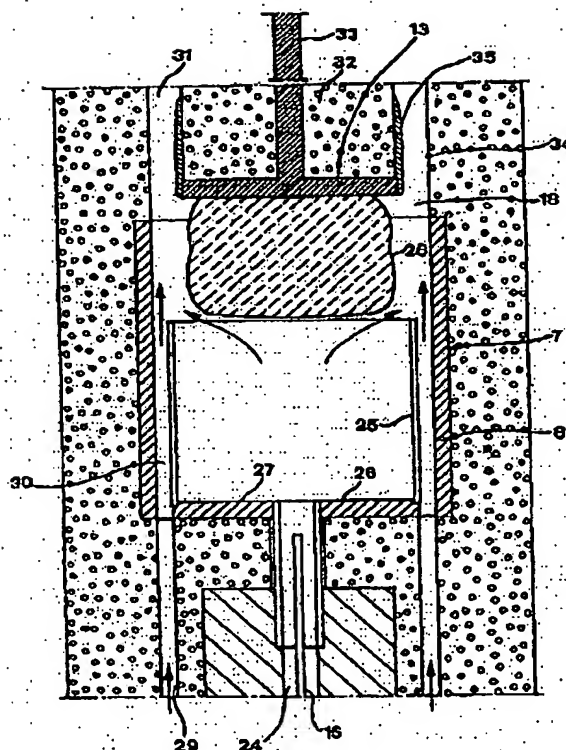


Figure 2

3/6

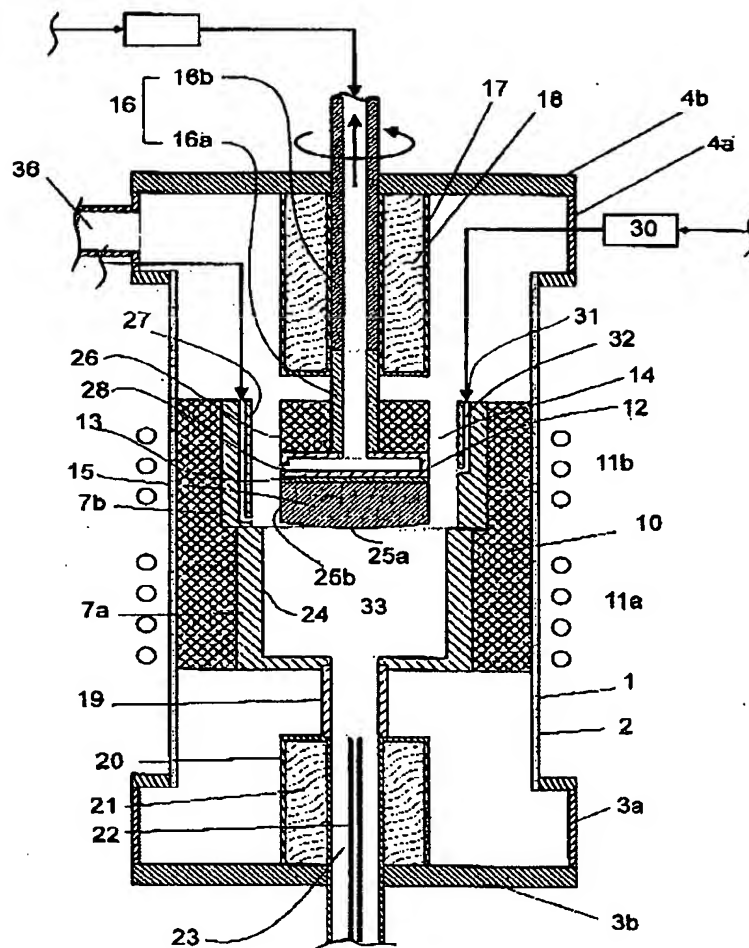


Figure 3

4/6

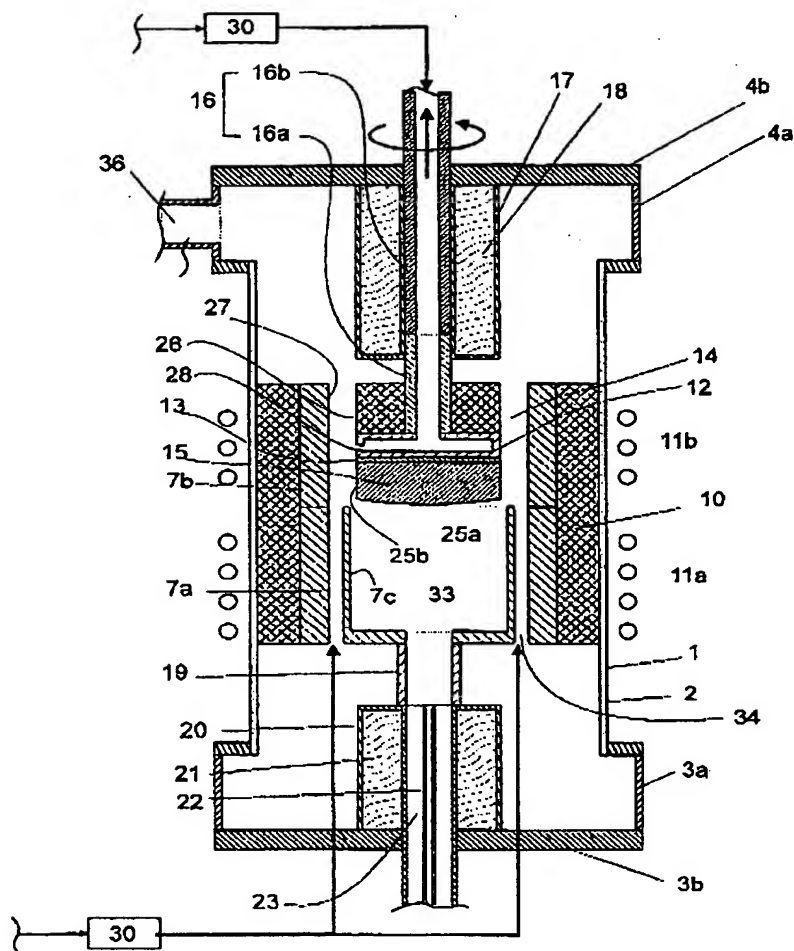


Figure 4

5/6

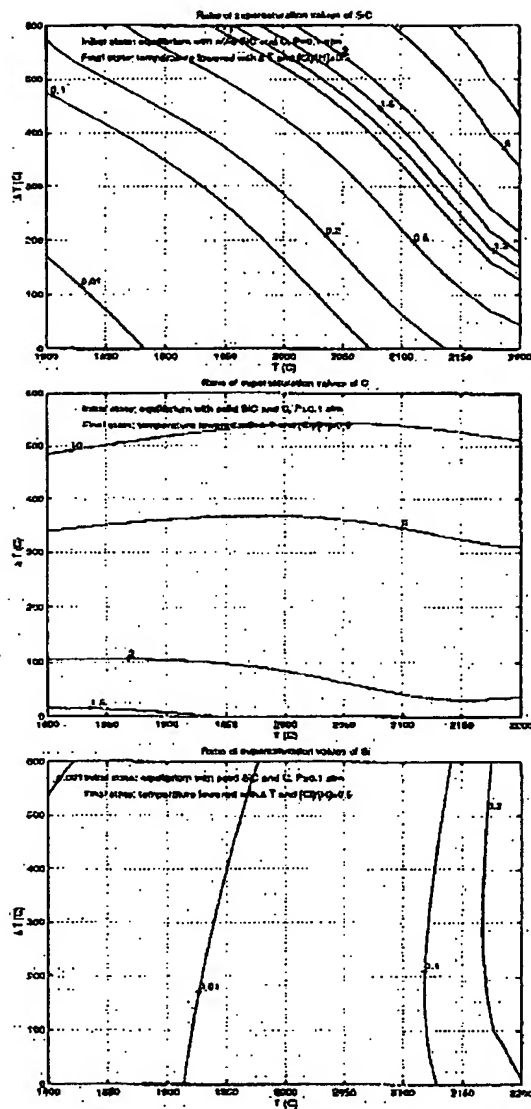


Figure 5

6/6

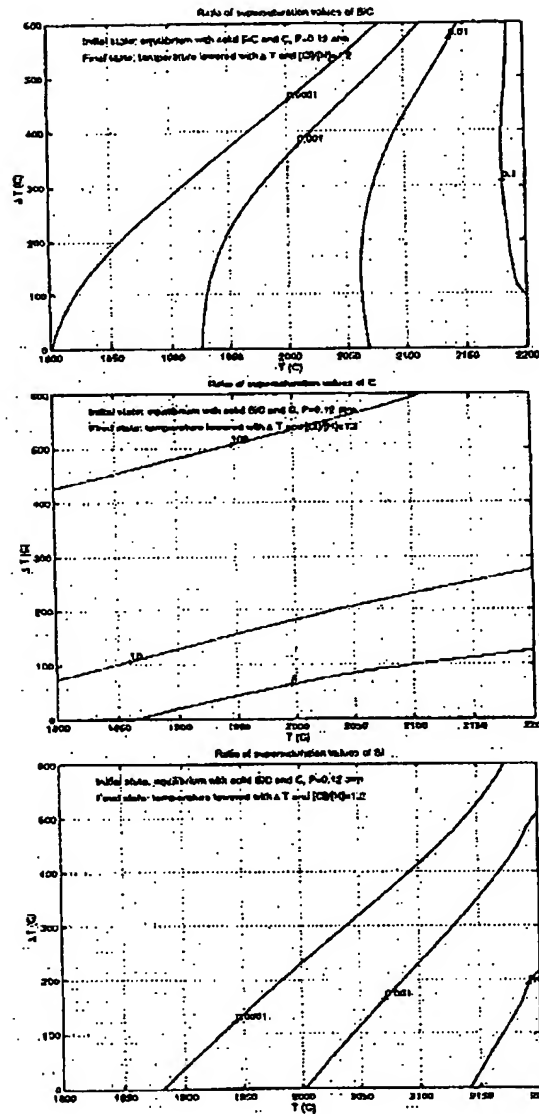


Figure 6